

On Some
Para-Hydroxytriphenylmethane
Derivatives

A Contribution to the Chemistry of
Free Radicals

BY

R. L. JICKLING

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Ann Arbor
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Para-Hydroxytriphenylmethane
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A Contribution to the Chemistry of
Free Radicals

A THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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R. L. JICKLING

1914

I beg to acknowledge the painstaking care with which Professor M. Gomberg has directed me in my work and I wish to express to him my great appreciation for all that he has helped me to accomplish.

ROBERT LEE JICKLING.

ANN ARBOR, MICH.,
November 13, 1914.



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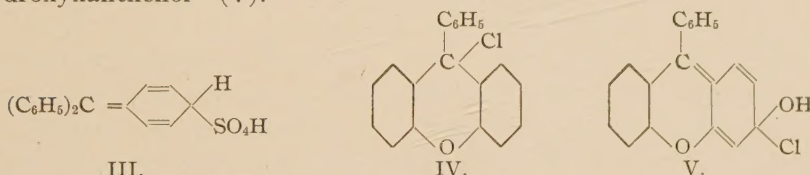
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I. Introduction.

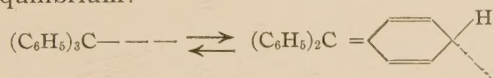
It was suggested by Kehrmann¹ and proved by Gomberg² through experimental evidence that the triarylmethyl halides exist in two forms, the benzoid as colorless and the quinoid as colored, and that there is a tautomeric equilibrium between the two:



In solution the presence of these two forms is evident, but in the solid state only the one, the benzoid, has been isolated. In the cases of the triarylmethyl sulfates³ (III), perchlorates,⁴ etc., the other desmotropic form constitutes the solid phase, *i. e.*, these derivatives are obtained only in the colored, quinoid state. The halides⁵ of the xanthenols and thioxanthenols, which after all are but triarylmethyl derivatives, exist in some instances as colorless solids (IV), like simple triphenylchloromethane, and in others as colored, resembling the triarylmethyl sulfates. The latter case is illustrated by the chloride of phenyl-3-hydroxyxanthenol⁶ (V).



The same explanation of color formation has been applied to the free radicals themselves.⁷ Accordingly triphenylmethyl would exist in solution as the two forms of the free radical, the benzoid and the quinoid, in tautomeric equilibrium:



From any solvent triphenylmethyl crystallizes in the colorless form, but there are, however, certain analogs of triphenylmethyl, which exist as colored solids.⁸

In each of the three series mentioned—the halides, the sulfates, and the free radicals—one and only one of the two forms has been isolated as a solid, in some cases the benzoid and in others the quinoid. Lately it was shown that a hydroxy group in the para position to the central carbon atom increases greatly the tendency toward tautomerization to the quinoid state.⁹ Triphenylcarbinol is known only in the benzoid form; its *p*-hydroxy derivative, however, has been obtained by Gomberg¹⁰ in two distinct forms, the colorless and the colored, separable from each other and either readily changeable into the other merely

by choice of suitable solvent. The significance of this latest fact becomes evident at once. The conception of the tautomeric existence of all other triarylmethyl derivatives in these two forms becomes more certain than before as the result of the conclusive proof that this one series, the carbinols, actually exists in the two desmotropic forms.

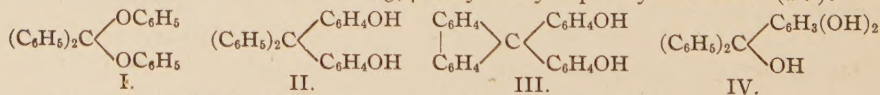
In view of these facts, the questions naturally arise: What influence would a *p*-hydroxyl group in triphenylmethyl exert as regards the tendency of the free radical toward tautomerization? Would *p*-hydroxytriphenylmethyl, like the simple triphenylmethyl, exist as two forms in solution only, and as a solid, colorless? Would the proportion of the quinoid tautomer in solution be greater than in the case of triphenylmethyl? Would this *p*-hydroxylated free radical exist even as a solid in the two desmotropic forms, as is the case with the corresponding carbinol? Or might the quinoid form of the *p*-hydroxytriphenylmethyl be the only one obtainable in the solid state?

As a related problem, we have also attempted to prepare *p*-hydroxytriphenylmethyl ether, the existence of which has been the subject of considerable discussion in recent literature.

For the preparation of the free radical and of the ether, *p*-hydroxytriphenylcarbinol must serve as the starting point. The methods previously used to prepare this carbinol are both tedious and extended. A far simpler synthesis has been devised during the course of this work, and since this method has proved to be efficacious in the preparation of many homologous hydroxy derivatives, a detailed study of the same has been undertaken.

II. The Reaction between Benzophenone Chloride and Phenol.

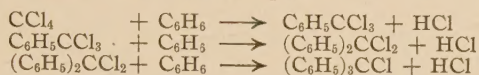
In an unsuccessful attempt to prepare diphenoxydiphenylmethane (I) by the reaction of sodium phenoxide on benzophenone chloride, Mackenzie¹¹ obtained instead di-*p*-hydroxytetraphenylmethane (II). He also noticed that the same product resulted from the direct action of phenol itself on benzophenone chloride. Through use of an analogous reaction, Smedley¹² prepared di-*p*-hydroxydiphenyldiphenylenemethane (III), from fluorenone chloride and phenol. Zincke¹³ made use of the reaction mentioned by Mackenzie, and obtained the same di-*p*-hydroxytetraphenylmethane, using a large excess of phenol and heating on the water bath for three days. Sachs and Thonet¹⁴ have condensed benzophenone chloride with catechol by means of absolute sulfuric acid, and claim to have obtained 3,4-dihydroxytriphenylcarbinol (IV).



A careful study of the reaction between benzophenone chloride and phenols has been undertaken and it has been found that the condensation

takes place in several successive steps. By observing the proper conditions, certain intermediary products of this reaction have been isolated, and in this way there has been devised a valuable and advantageous method of preparing various hydroxytriphenylcarbinols.

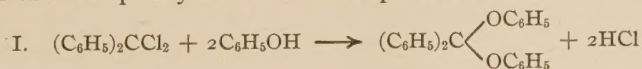
The Preparation of Benzophenone Chloride.—In studying the Friedel and Crafts' synthesis, Boeseken¹⁵ found that the reaction between carbon tetrachloride and benzene under the influence of the catalyst, aluminium chloride, proceeds in at least two steps:



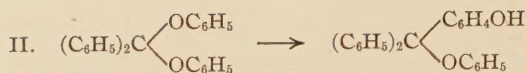
He was unable to isolate benzotrichloride, but by using an excess of carbon tetrachloride he obtained benzophenone chloride in good yield. We desire to emphasize the value of this reaction as an excellent means for the preparation of benzophenone chloride in large quantities.

We have obtained benzophenone chloride in 90 per cent. yields by observing the following procedure: In a wide-mouth, two-liter bottle, 135 grams (1 mol.) finely-divided aluminium chloride are suspended in 300 cc. carbon tetrachloride. To this are added through the course of an hour or more, 156 grams (2 mol.) benzene mixed with about an equal volume of carbon tetrachloride. By proper cooling and shaking the reaction mixture should be kept below 30°. The following morning the granular mass, consisting of the double salt of the keto-chloride and aluminium chloride, is decomposed in the same bottle, preferably glass-stoppered, by adding a considerable quantity of ice and shaking vigorously. The temperature of the mixture is lowered to such an extent by the ice and the hydrochloric acid set free that hydrolysis of the benzophenone chloride is reduced to a minimum. The carbon tetrachloride solution, after drying over calcium chloride, is concentrated and the residue distilled in vacuum. The resulting product contains, as a rule, 90 to 95 per cent. benzophenone chloride, the balance being benzophenone. Redistillation in vacuum after addition of the calculated amount of phosphorus pentachloride gives pure benzophenone chloride.

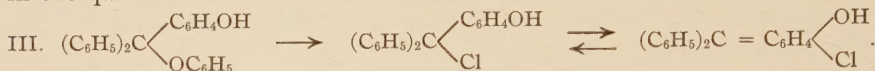
Mechanism of the Reaction.—The reaction between benzophenone chloride and phenol proceeds, as previously mentioned, in several successive steps. The first stage in all cases consists most probably in the formation of the diphenyl ether of benzophenone:



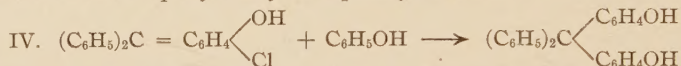
Secondly, under the influence of the hydrogen chloride present, this diphenoxy compound suffers an intramolecular rearrangement with respect to but one of the phenoxy groups:



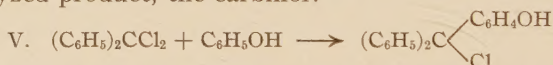
The resulting phenyl ether, like all similar compounds, must be easily decomposed by hydrogen chloride with the formation of the chloride of *p*-hydroxytriphenylcarbinol, which, as Gomberg has shown, exists only in the quinoid state.



And thirdly, at elevated temperatures this fuchstone hydrochloride reacts readily with more phenol—the final step of the reaction—with the production of di-*p*-hydroxytetraphenylmethane:



The reasons which force us to interpret the entire reaction according to this above scheme are as follows: (1) It has been found possible to adjust the conditions of the experiment—presence of solvent—so as to obtain only diphenoxydiphenylmethane as the final product (Equation I). (2) Either by starting with this diphenoxy compound and exposing the same to hydrogen chloride (Equation II), or by carrying out the condensation of benzophenone chloride and phenol in the absence of solvent and at a sufficiently low temperature, we have obtained as the main product *p*-hydroxytriphenylcarbinolchloride, isolated as its hydrolyzed product, the carbinol:



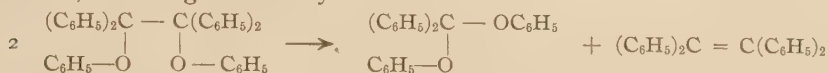
(3) Furthermore, we have found that the di-*p*-hydroxytetraphenylmethane is formed not only by heating benzophenone chloride with phenol as Mackenzie observed, but also by the transformation of diphenoxydiphenylmethane or by condensation of *p*-hydroxytriphenylcarbinolchloride with phenol (Equation IV).

Thus it can be seen, that this reaction lends itself not only for the preparation of the tetraphenyl compound, as Mackenzie found, but also for preparing diphenoxy derivatives and *p*-hydroxytriphenylcarbinols. The usefulness of this reaction becomes apparent when we take into consideration its wide applicability, its simplicity, and the yields of the products obtained. And in all these we feel that it is superior to the previously described syntheses.

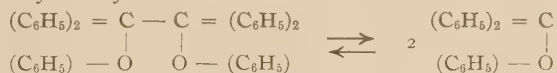
Diphenoxydiphenylmethane.—Mackenzie¹¹ in his attempts to prepare diphenoxydiphenylmethane did not follow the reaction between benzophenone chloride and phenol in any other solvent than an excess of phenol and for this simple reason failed. By carrying out the above reaction in benzene we have prepared the diphenoxy compound. Molten

phenol was added slowly to an equal weight of benzophenone chloride mixed with a considerable volume of benzene, the reaction mixture being kept at about 50°. A stream of dry air was drawn, under slight vacuum, through the mass to remove the hydrogen chloride as formed, and thus prevent the decomposition as well as the rearrangement of the diphenoxy derivative. Concentration of the benzene solution and addition of petroleum ether gave the diphenoxydiphenylmethane in clusters of white needles melting at 132°, after recrystallization from alcohol. The yield was about 85 per cent. of the calculated amount.

Wieland¹⁶ described as diphenoxydiphenylmethane a compound which he had obtained by heating the diphenyl ether of benzpinacone to 280°, resulting assumably as follows:



A sample prepared according to Wieland's method was found to be identical with the product from the reaction of benzophenone chloride and phenol in benzene solution. The melting point of a mixture of the two corresponds to that of either product, 132°. Thus our results corroborate Wieland's conclusion as regards the constitution of the diphenoxy derivative. Consequently they also lend support to his conception of the constitution of the above mentioned diphenyl ether of benzpinacone and that of its dissociation product, the corresponding free radical, diphenylphenoxymethyl:¹⁷



Diphenoxydiphenylmethane is far more stable than dimethoxydiphenylmethane and its homologs, which as described by Mackenzie suffer decomposition even upon exposure to air. Neither boiling water nor normal alkali has any effect upon the diphenoxy derivative. On the other hand, like its analogs, diphenoxydiphenylmethane is hydrolyzed by dilute acids, even by acetic acid, into benzophenone and the corresponding alcohol, *i. e.*, in this case, phenol. When exposed to hydrogen chloride, as has been previously mentioned, it undergoes intramolecular rearrangement, forming either triphenyl- or tetraphenyl derivatives according to the conditions. In a quantitative experiment 1.45 grams of substance gave, when exposed to an atmosphere of dry hydrogen chloride at room temperature, 0.67 gram *p*-hydroxytriphenylcarbinol but *no* di-*p*-hydroxytetraphenylmethane. A 3 gram sample, when treated similarly but at 50°, gave 1.3 grams of the carbinol and 0.5 gram of the tetra compound together with some unchanged diphenoxy derivative. The significance of this latter result will be brought out below under a discussion of the formation of the tetraphenyl derivative.

The Preparation of *p*-Hydroxytriphenylcarbinol

Bistrzycki and Herbst¹⁸ first prepared *p*-hydroxytriphenylcarbinol through elimination of carbon monoxide from *p*-hydroxytriphenylacetic acid by means of concentrated sulfuric acid. This step is accomplished with satisfactory yield although the preparation of the acid by condensation of mandelic acid with phenol involves a rather laborious process. Baeyer and Villiger¹⁹ obtained the identical product by demethylating *p*-methoxytriphenylcarbinol by boiling the latter in a mixture of acetic and sulfuric acids for twelve hours, the methoxy carbinol having been prepared by Grignard's synthesis from anisic ester and phenyl bromide. Gomberg²⁰ demethylated the methoxy carbinol by means of aluminium chloride in benzene solution, a method which gives at the same time more or less diphenylquinomethane and other by-products. A highly satisfactory method of preparing this carbinol is offered by the reaction of benzophenone chloride and phenol under the following conditions.

Molten phenol (4 mol.) is chilled in a flask in such a way as to be evenly distributed on the interior surface. Benzophenone chloride (1 mol.) is then added, the mouth of the flask being protected by a calcium chloride tube. The reaction begins at once with evolution of hydrogen chloride, and an occasional rotation of the flask brings fresh portions of the phenol into reaction. After ten hours or more at a temperature between 20 and 25°, the mass is subjected to steam distillation in the same flask to remove the excess of phenol. The residue is digested with five per cent. alkali and the alkaline solution extracted* with ether in order to remove any benzophenone which may be present. After filtration the dissolved ether is removed from the alkaline solution by a stream of air. Addition of ammonium chloride or treatment with carbon dioxide liberates the carbinol and the dihydroxy-tetraphenyl compound in the form of a paste, which changes on standing to a granular mass. As a means of separation of the carbinol from the tetraphenyl derivative either alcohol or 95 per cent. acetic acid may be used, as the latter product is soluble in either solvent to an extent of not more than 0.1 gram in 100 cc. Using about 6 cc. alcohol to each gram of the mixed products dissolves the carbinol and leaves a fine suspension of the tetra compound. The filtration, often quite troublesome, may be facilitated

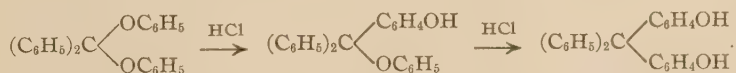
* This extraction is necessary at this point not only to remove the benzophenone in suspension but also the benzophenone held in solution by the sodium salt of the carbinol. The solubility of benzophenone under these conditions has been verified by a blank experiment in which it was found that benzophenone, insoluble itself in alkali, was jointly soluble with the carbinol in *n*-NaOH. In the extraction a large amount of ether is to be avoided since the carbinol through hydrolysis of its salt is also removed to some extent by this solvent.

by the addition of a few cc. of a concentrated aqueous solution of sugar. Addition of water and a few drops of ammonium hydroxide to the alcoholic filtrate precipitates the carbinol in a beautiful crystalline form. Though hardly essential the carbinol may be recrystallized from benzene in order to remove traces of the tetraphenyl derivative.

Following the above method we have obtained with samples of 12 to 18 grams of benzophenone chloride yields of 90 to 98 per cent. of the calculated amount of the carbinol, with but a few hundred milligrams of the by-product, di-*p*-hydroxytetraphenylmethane. The difficulty of controlling the temperature of the viscous reacting mixture may cause at times the formation of a gram or more of the tetra compound and a corresponding decrease in the yield of carbinol. Adoption of the above method was the result of a series of experiments in which the temperature and the time of reaction, as well as the relative amounts of benzophenone chloride and phenol, were varied. A few typical examples, tabulated below, will make evident the reasons for the selection of the described procedure as the one most probable to give a maximum yield of the carbinol from a given quantity of benzophenone chloride.

Chloride.	Phenol.	Temperature.	Time.	Carbinol.	"Tetra."
12 g.	16 g.	90°	2 hrs.	0 g.	16 g.
12	3.6	90	4	3.6	0
12	10	40-50	1	8.7	0.2
12	20	0-20	1	8.0	0.3
12	17	25-35	1	10.8	1.8
12	20	20-25	15	13.4	1.2

Di-p-hydroxytetraphenylmethane.—As has been described in part, di-*p*-hydroxytetraphenylmethane results (1) from the action of dry hydrogen chloride on diphenoxydiphenylmethane, (2) from the condensation of *p*-hydroxytriphenylcarbinol and phenol, using hydrochloric acid as a catalyst, or (3) from the reaction of benzophenone chloride and phenol at high temperatures. In the first case we may account for its formation by assuming a double intramolecular rearrangement.

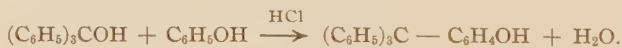


Against this interpretation stands the objection that we have been unable to isolate the intermediary mono-phenyl ether (II), but have found that instead of this product, *p*-hydroxytriphenylcarbinol chloride and phenol are produced. Consequently the tetraphenyl derivative must result from the condensation of these two products upon heating. That such may be the case has been actually verified by the following experiment: Hydrochloric acid gas was passed into a mixture of 4 grams *p*-hydroxytriphenylcarbinol and 10 grams phenol at 50° and after

a short time 3.5 grams of the tetra compound were isolated. In acetic acid solution, 3 grams carbinol and 3 grams phenol gave, after passing in hydrogen chloride, 2.8 grams of the tetraphenyl derivative. As regards the third method, Zincke heated three parts of benzophenone chloride with four of phenol on the steam bath for three days. According to our experience, this reaction is practically completed at the end of but a few hours with a 90 per cent. yield of the tetraphenyl compound.

Di-*p*-hydroxytetraphenylmethane crystallizes from acetic acid in glistening, white flakes or needles, melting at 286° without decomposition. It forms a di-acetyl derivative by boiling in three times its weight of acetic anhydride together with a small amount of sodium acetate.

Mono-p-hydroxytetraphenylmethane.—Finding the reaction between *p*-hydroxytriphenylcarbinol and phenol to proceed so readily, we concluded that we were dealing not with a case of anhydrolysis but with one of condensation under the influence of a catalyst. The correctness of this inference was then tested in the case of mono-*p*-hydroxytetraphenylmethane which Baeyer and Villiger²¹ had prepared by treating triphenylcarbinol and phenol in acetic acid solution with a large quantity of concentrated sulfuric acid. Our experience has shown that a dehydrating agent is not essential in order to bring about this condensation. Upon addition of 1 cc. of concentrated hydrochloric acid to 2 grams triphenylcarbinol and 3 grams phenol, heated on the water bath, the tetraphenyl derivative began to separate in a short time, and at the end of 15 minutes 2.2 grams of this compound had formed. It gave a melting point of 282° , as Baeyer and Villiger found. Similarly, one drop of sulfuric acid gave even better yields, while in benzene solution the carbinol and phenol condensed quantitatively in a short time under the influence of but one drop of sulfuric acid.



The ease with which the *p*-hydroxyphenyl group is introduced stands in sharp contrast with the difficulties encountered in the preparation of the hydrocarbon tetraphenylmethane with its four *phenyl* groups. This curious fact is as yet unaccounted for, the theory of steric hindrance being inadequate to explain this difference.

III. Concerning the Free Radical, *p*-Hydroxytriphenylmethyl.

The general method for the preparation of free radicals in the triarylmethyl series consists in subjecting the triarylmethylcarbinol halide to the action of metals.



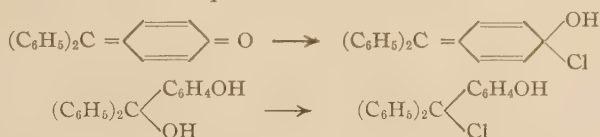
Often the free radical thus produced exists wholly in the monomolecular form, as indicated by the above equation. In other instances there is,

without doubt, an equilibrium between the monomolecular and the dimolecular forms:*



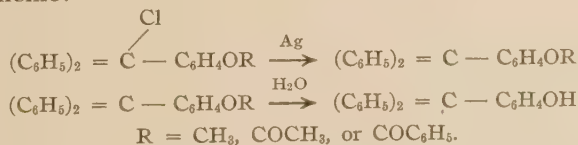
This equilibrium is influenced in each particular case by the temperature, by the nature of the solvent, as well as by the constitution of the radical itself. In this paper when speaking of free radicals, the existence of such an equilibrium is to be understood.

Unfortunately *p*-hydroxytriphenylcarbinol chloride²² presents an exception to the general reaction employed in preparing free radicals. This had also been found to be the case with the chlorides of *p*-hydroxybenzo- γ -pyranols²³ and of *p*-hydroxyxanthenols.²⁴ The cause for this exceptional behavior we believe to be the same in all cases, namely, the chlorine and the hydroxyl group are linked to one and the same carbon atom in these carbinol chlorides. The formation of the above *p*-hydroxy chloride takes place by exposing in the solid form either fuchsone or one of the two isomers of *p*-hydroxytriphenylcarbinol to gaseous hydrochloric acid. The resulting products are identical hence we must assume the usual equilibrium between two tautomeric isomers.



On treatment with molecular silver a molecule of *hydrogen chloride* is split off instead of the usual single chlorine atom, giving consequently fuchsone and not the free radical, *p*-hydroxytriphenylmethyl.

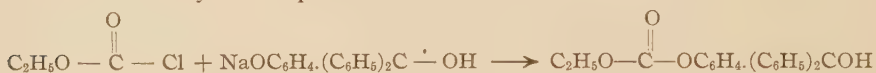
From these results it became evident that the only procedure for the study of the free radical would come through protection or alteration of the *p*-hydroxyl group. It had been previously found that, while the hydroxyl group in the *p*-position tended to force the tautomeric equilibrium toward the quinoid form, the methoxy, the acetoxy, and the benzoxy group in the same position, on the other hand, cause their derivatives to exist only in the benzoid form. Consequently it was considered entirely feasible to prepare the free radical from the corresponding stable chlorides, and the free hydroxy-radical according to the following scheme:



* As regards the constitution of the dimolecular modification of the free radical, some assume it to be a molecularly associated complex of the free radical, while others consider it as a hexarylethane, readily suffering dissociation into its halves.

Realizing, however, the difficulties usually encountered in the removal of any of these protecting groups, we turned first to the carboalkoxy groups, used so extensively and successfully by Emil Fischer²⁵ as a temporary protection of hydroxyl groups, in his recent studies on tannins. A carboalkoxy group affects tautomerization advantageously by forcing its derivatives into the benzoid form, and is readily removed through hydrolysis, thus restoring the hydroxy compound.

p-Carboethoxytriphenylcarbinol.—14 grams *p*-hydroxytriphenylcarbinol are dissolved in 55 cc. *n*-NaOH and a considerable amount of ice added to the solution. To the suspension of the sodium salt of the carbinol are added with vigorous stirring 6 grams (1.1 mol.) chlorcarbonic ester. The resulting stiff paste upon becoming granular is filtered out. After drying partially, the product is recrystallized from alcohol by addition of water. The yield is quantitative.



p-Carboethoxytriphenylcarbinol is readily soluble in benzene, ether, etc., crystallizing from these solvents upon addition of petroleum ether as white needles, melting at 119°.

p-Carboethoxytriphenylcarbinol Chloride.—According to the usual method of preparing triarycarbinol chlorides, this chloride is formed by passing gaseous hydrochloric acid into a benzene solution of the carbinol in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride, which after washing with a mixture of ether and petroleum ether, melt at 98°.

Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_3\text{Cl}$: Cl, 9.67. Found: Cl, 9.62.

The Action of Metals.—As has been mentioned, the usual result of the action of molecular silver or other metals on the chlorides of the triarylcarbinols in solution is the formation of the free radical with carbon in the trivalent state. The unsaturated nature of this class of compounds is illustrated, among others by the avidity with which they unite with oxygen to form peroxides.



So characteristic is this reaction, that the isolation of the peroxide is now generally accepted as sufficient evidence of the existence of the corresponding free radical, though even temporary. Tested in this manner the carboethoxy-chloride gives rise unquestionably to its free radical.

p-Carboethoxytriphenylmethyl Peroxide.—When treated with molecular silver out of contact with air a benzene solution of *p*-carboethoxytriphenylcarbinol chloride assumes after several hours a dark, cherry-red

color. On exposure to air this color disappears in a way analogous to that in the case of triphenylmethyl. Evaporation of the filtered benzene solution and washing the residue with ether to remove any unchanged chloride gives a relatively small amount of the peroxide, which when recrystallized from benzene melts at 171° . Much better yields of the peroxide result from boiling the chloride and silver in benzene with a stream of dry air passing through the solution. Like other triaryl peroxides, *p*-carboethoxy-peroxide is but slightly soluble in benzene and nearly insoluble in ether.

Calculated for $C_{44}H_{38}O_8$: C, 76.05; H, 5.52; Mol. Wt., 694.

Found: C, 75.73; H, 5.56; Mol. Wt., 701.

All attempts to obtain the dihydroxy-peroxide by removing the carboethoxy groups alone in this peroxide resulted in the splitting of the product either to *p*-carboethoxytriphenylcarbinol or to *p*-hydroxytriphenylcarbinol. Warming the solution of the peroxide in a mixture of acetic and sulfuric acids (4:1) gives the former carbinol in good yield. The peroxide is not affected by boiling *n*-NaOH, but sodium ethoxide or a solution of potassium or barium hydroxides in methyl alcohol decomposes it to the hydroxy-carbinol.

Isomerization of the Free Radical.—The formation of the above-described peroxide proves definitely that the free radical, *p*-carboethoxytriphenylmethyl, is formed as the initial step of the reaction between the chloride and molecular silver. We next attempted to isolate the unsaturated free radical in the solid state by concentration of the colored solution of the same in an atmosphere of carbon dioxide. But the residue thus obtained proved to be colorless, was found to be entirely devoid of unsaturated properties, and would no longer yield a peroxide on exposure to air, either as the solid or in solution. Consequently we may assume that the free radical exists only temporarily, and must have been affected in some way during the subsequent stages of its isolation. In fact, even in the preparation of the peroxide through simultaneous action of silver and air upon the chloride, there is formed as a coating on the silver more or less of this colorless, saturated compound in addition to the peroxide. More of this substance, and relatively less of the peroxide, is obtained if the solution of the free radical is kept for some time previous to oxidation; still more, if the solution is heated. It is thus not surprising that we find upon boiling the benzene solution of the chloride with silver for several hours, that practically none of the peroxide can then be obtained. For under such treatment, the reactive free radical is transformed completely into this colorless, inert substance.

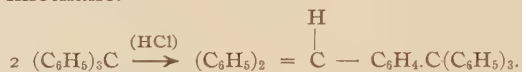
This new product is a white, amorphous powder insoluble in ether and but slightly soluble in boiling benzene or acetic acid. It melts

at about 280° without decomposition. A sample from the last-mentioned solvent gave an analysis corresponding closely to that calculated for the free radical. A molecular weight determined according to the method of Menzies²⁶ proved, however, to be approximately twice that of the free radical.

Calculated for $C_{22}H_{19}O_3$: C, 79.72; H, 5.78; Mol. Wt., 331.

Found: C, 79.36; H, 6.04; Mol. Wt., 680, 664.

The above results indicate that this unsaturated compound is either produced from the monomolecular free radical through polymerization, or more likely, is a metamer resulting from transformation of the dimolecular modification of the free radical. A change of this kind has been proved to take place in the case of the simplest free radical in this series, namely, triphenylmethyl. It was shown by Gomberg²⁷ that this dimolecular free radical is changed in benzene under the influence of hydrochloric acid, as a catalyst, to a stable isomer, the constitution of which has been definitely determined by Chichibabin²⁸ as *p*-benzhydryltetraphenylmethane.



Later Schlenk²⁹ found that this same transformation is brought about by the action of metallic sodium on the free radical in ether solution.

The question arises: May not a similar metamerization take place spontaneously in the case of certain other radicals? In other words, may not the change of the free radical to its stable isomer proceed even without the presence of a catalyst? We consider this entirely possible, and, at the present time, this is the most plausible explanation that we can offer for the relatively impermanent existence of the free radical, *p*-carboethoxytriphenylmethyl. We have modified the methods in attempting to prepare this radical by various means—by employing different solvents, by using mercury or copper instead of silver, by concentrating the solutions at very low pressure and temperature—but the result has invariably been the formation of the same stable metamer of the free radical.

Acetoxy- and benzoxytriphenylmethyl chlorides behave in this respect entirely analogously to the carboethoxy-chloride. They, too, give free radicals which isomerize to stable metamers. The occurrence of such spontaneous transformation we believe to be far more frequent than has been assumed in the past. The apparent non-existence of the free radicals, tri-*p*-tolylmethyl, di-*p*-tolylphenylmethyl, *p*-tolylldiphenylmethyl,³⁰ tri-*p*-anisylmethyl,³¹ etc., may be explained as due to a similar cause, namely, to isomerization.

p-Benzoxytriphenylcarbinol.—Following the Schotten-Baumann reaction, 14 grams *p*-hydroxytriphenylcarbinol are dissolved in an excess

of *n*-NaOH, 14 grams benzoyl chloride added and the mixture thoroughly shaken for some time. The resulting oily precipitate solidifies on standing. Its benzene solution is extracted with 10 per cent. alkali and dried over calcium chloride. Addition of petroleum ether gives the benzoxy-carbinol in the form of small crystals, melting at 132° after recrystallization from glacial acetic acid. We have nothing to add to the properties as given by Bistrzycki and Herbst.³²

p-Benzoxytriphenylcarbinol Chloride.—This chloride is prepared by saturating a benzene solution of the carbinol with hydrogen chloride in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride in nearly quantitative yield, melting point 105° .

Calculated for $C_{26}H_{19}O_2Cl$: Cl, 8.90. Found: Cl, 8.74.

p-Benzoxytriphenylmethyl Peroxide.—With molecular silver, a solution of the benzoxy-chloride gives the usual deep color of a free radical. On evaporation of this solution, however, a mixture of two substances is obtained, the one the inert isomer of the free radical and the other the peroxide. For identification the latter was prepared by simultaneous action of silver and oxygen on the chloride. The peroxide is slightly soluble in boiling benzene, nearly insoluble in ether, and melts at 167° with decomposition. This peroxide is also readily hydrolyzed to its corresponding carbinol by warming in a mixture of acetic and sulfuric acids.

Calculated for $C_{52}H_{38}O_6$: C, 82.29; H, 5.05. Found: C, 82.40; H, 5.40.

As in the case of *p*-carboethoxytriphenylmethyl, we were unable to isolate the free radical, *p*-benzoxytriphenylmethyl. On boiling the chloride and silver in benzene, the resulting highly-colored solution of the free radical loses its color, even during concentration, with the formation of the colorless isomer. A sample of the latter, recrystallized from acetic acid, melted at $266-9^{\circ}$, and gave an analysis and molecular weight corresponding closely to that calculated for the dimolecular free radical.

Calculated for $C_{52}H_{38}O_4$: C, 85.92; H, 5.27; Mol. Wt., 726.

Found: C, 85.70; H, 5.55; Mol. Wt., 710.

p-Acetoxytriphenylcarbinol.—The following procedure has been adopted for the preparation of this carbinol: 20 grams of *p*-hydroxytriphenylcarbinol and 3 grams of anhydrous sodium acetate are boiled for two hours in 50 grams acetic anhydride. The product is precipitated by pouring the above solution into 100 cc. water and, if necessary, may be recrystallized from acetic acid. It possesses the properties described by Bistrzycki³³ for this carbinol.

p-Acetoxytriphenylcarbinol Chloride.—Gomberg³⁴ has prepared this chloride by the usual method, using calcium chloride as a dehydrating

agent. We find it advisable to avoid the use of hydrogen chloride. The carbinol is suspended in an excess of acetyl chloride (2:3 mol.) and the mixture heated until all goes into solution. The excess of solvent is removed by careful heating. Upon the gradual addition of petroleum ether and allowing to stand, the acetoxy-chloride separates out slowly as white needles, melting at 88°. It is very soluble in benzene or ether but only slightly so in petroleum ether.

Calculated for $C_{21}H_{17}O_2Cl$: Cl, 10.53. Found: Cl, 10.52.

p-Acetoxytriphenylmethyl Peroxide.—This peroxide must be prepared by the simultaneous action of silver and oxygen on the chloride in solution. The resulting product, after recrystallization from benzene and ether, melts at 172°. It is readily hydrolyzed to the corresponding carbinol.

Calculated for $C_{42}H_{34}O_6$: C, 79.46; H, 5.40.
Found: C, 79.67; H, 5.80.

In an analogous way, the acetoxy polymer was prepared as a white, amorphous powder, the purification of which gave a product melting with decomposition at 255–270°. In its low solubility, its non-conversion through hydrolysis into the corresponding carbinol, and its lack of unsaturated properties, this polymer resembles the other analogs as described.

IV. Concerning *p*-Hydroxytriphenylmethyl Ether.

A number of compounds, presumably triarylmethyl ethers, have been described in the literature, but it was recently shown³⁴ that these products could not possess the constitutions attributed to them. On certain negative results, Schlenk³⁵ concluded that the simplest member of this series, triphenylmethyl ether, is apparently incapable of existence. Gomberg,³⁴ on the other hand, has worked out a method by means of which this substance, as well as its analogs, can be prepared, and has found that these ethers or oxides possess a fair degree of stability.

A product described as *p*-hydroxytriphenylmethyl ether³⁶ appeared especially doubtful on the evidence presented. On account of the ease of hydrolysis of the carboethoxy group, the preparation of the corresponding ether seemed to offer a ready means of obtaining this *p*-hydroxy-ether.

p-Carboethoxytriphenylmethyl Ether.—10 grams *p*-carboethoxytriphenylcarbinol chloride, 30 grams mercuric oxide and 50 cc. benzene are sealed and shaken for a month at room temperature. The resulting solution, after warming, is filtered from the mercuric oxide and chloride and concentrated. Upon addition of petroleum ether the product is precipitated as a yellow crystalline mass, which after recrystallization from benzene and absolute ether is white and melts at 219°.

Calculated for $C_{44}H_{38}O_7$: C, 77.84; H, 5.65; Mol. Wt., 678.

Found: C, 77.80; H, 5.74; Mol. Wt., 694.

The *p*-carboethoxy ether resembles other triaryl ethers, being very readily hydrolyzed by acids. Thus it is converted into the carbinol by boiling in acetic acid or in alcohol containing a few drops of sulfuric acid.

As a rule, the carboethoxy group is easily removed by cold dilute alkali or aqueous ammonia, acetone or pyridine being added if necessary to increase the solubility of the products.³⁷ Treated in this manner, *p*-carboethoxytriphenylmethyl ether does lose its carboethoxy groups, but unfortunately suffers further hydrolysis to *p*-hydroxytriphenylcarbinol. Various conditions and hydrolytic agents of alkaline nature have been employed but as yet it has been found impossible to remove only the carboethoxy groups and thus obtain the *p*-hydroxy-ether. It is reasonable to suppose that the first action of the hydrolysis does consist in the destruction of the carboethoxy groups, and the hydroxy-ether so produced must become further hydrolyzed in its turn. In other words this hypothetical ether, unlike other triarylmethyl ethers, is hydrolyzed to its carbinol not only in the presence of acid but also in the presence of alkali. It will be recalled that a similar behavior was met with in the case of the corresponding *p*-carboethoxytriphenylmethyl peroxide.

V. Summary.

1. A detailed study of the reaction between benzophenone chloride and phenol has been carried out. Contrary to previous reports in the literature, the reaction was found to proceed in several successive stages, and the mechanism of the reaction has been studied.

2. A simple and excellent synthetic method for the preparation of *p*-hydroxytriphenylcarbinol has been devised, a method which promises to become a valuable means for obtaining analogous compounds.

3. *p*-Hydroxytriphenylcarbinol chloride on treatment with metals gives up hydrochloric acid and not chlorine, thus making it impossible to prepare the corresponding free radical according to the usual method.

4. *p*-Carboethoxy-, *p*-benzoxy-, *p*-acetoxycarbinol chlorides do give the respective free radicals, but these were found to be too unstable to be isolated as such.

5. From the experimental facts obtained, an explanation is derived to account for the impermanent character of these free radicals, which may also serve to explain similar results previously reported by others.

6. It was found impossible to obtain *p*-hydroxytriphenylmethyl ether, by partial hydrolysis of its carboethoxy derivative, since at the same time the latter is hydrolyzed completely to *p*-hydroxytriphenylcarbinol.

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